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(54) **TIRE INCORPORATING A RUBBER COMPOSITION INCLUDING A SPECIFIC HYDROCARBON RESIN**

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(57) **ABSTRACT**

Described herein are tires comprising a rubber composition based on at least an elastomer and a hydrocarbon resin, wherein the hydrocarbon resin is based on a cyclic monomer selected from the group consisting of a distillation cut from a petroleum refinery stream, and/or C₄, C₅ or C₆ cyclic olefins and mixtures thereof, and wherein the hydrocarbon resin has a number average molecular weight (Mn) of between 150 and 800 g/mol, and a content of aromatic protons (H Ar, expressed in mol %), a glass transition temperature (Tg, expressed in ° C.), and a number average molecular weight (Mn, expressed in g/mol) that are represented by (1) H Ar≤6 mol %, (2) Tg≥95–2.2*(H Ar), (3) Tg≥125–(0.08*Mn).

14 Claims, 1 Drawing Sheet

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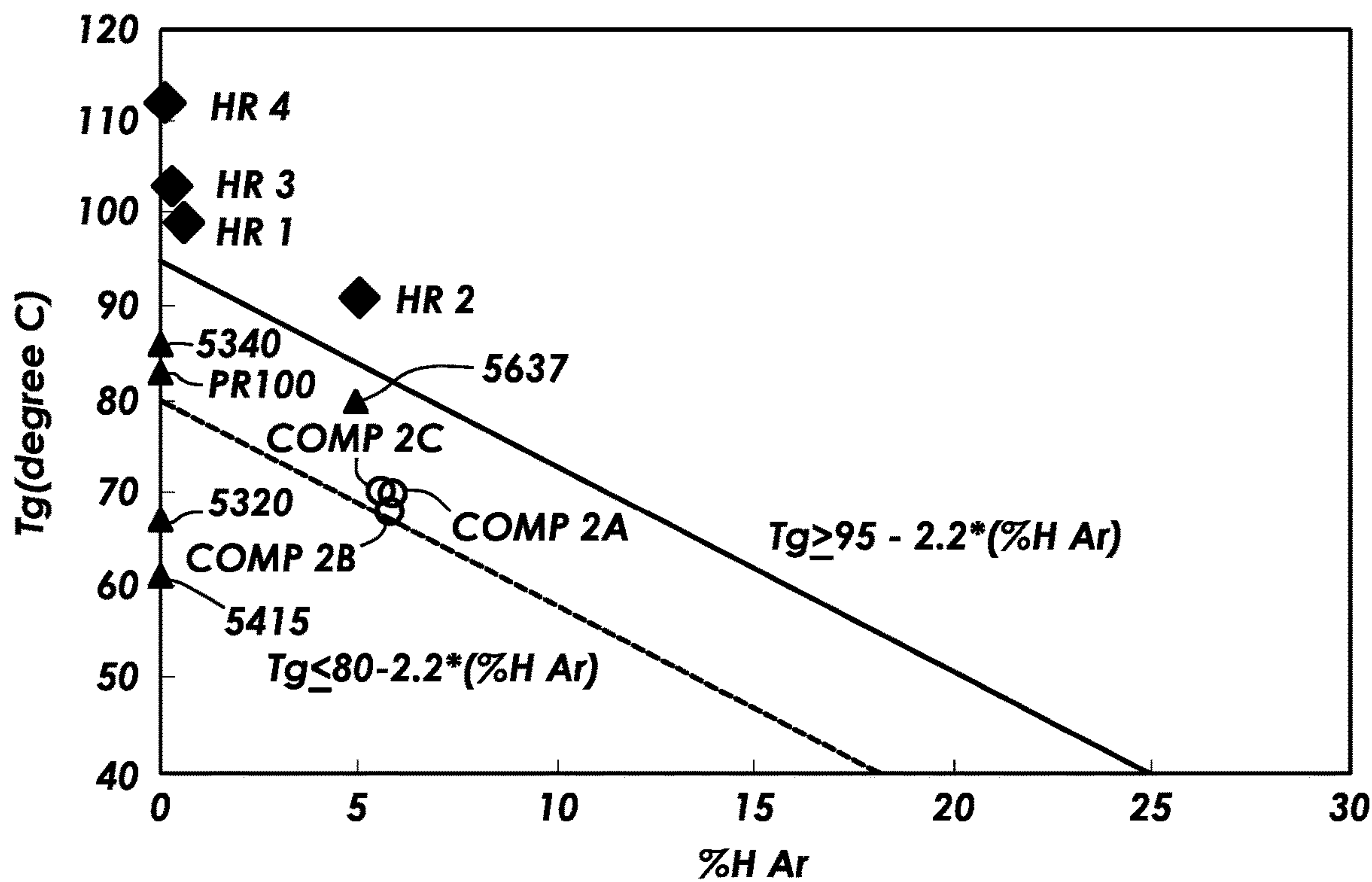


FIG.1

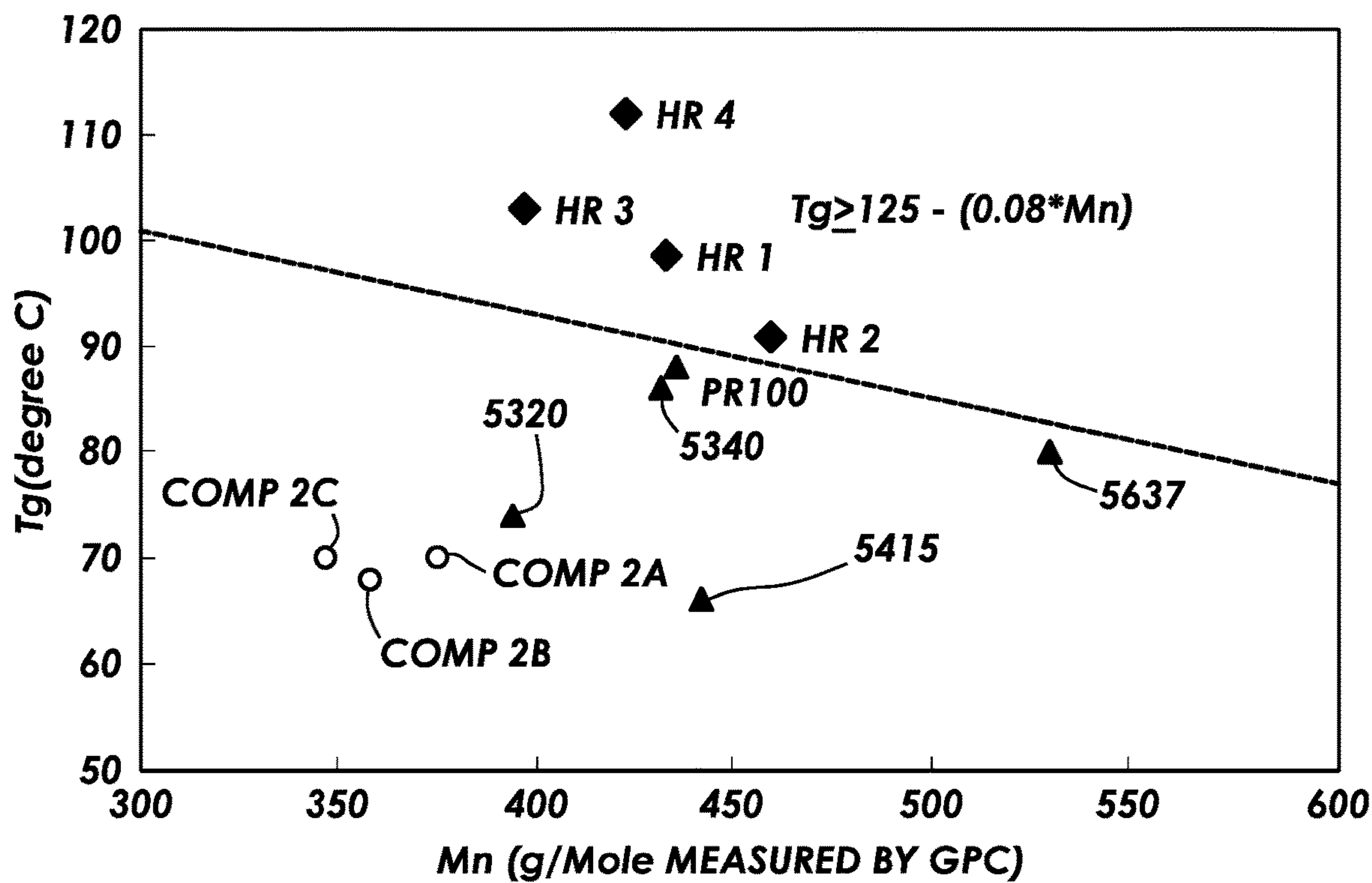


FIG.2

TIRE INCORPORATING A RUBBER COMPOSITION INCLUDING A SPECIFIC HYDROCARBON RESIN

BACKGROUND

The present invention relates to tires comprising rubber compositions comprising a specific hydrocarbon resin.

It is known from the prior art that elastomers having a low glass transition temperature ("Tg") enable an improvement in terms of abrasion performance (WO 2015/043902). These low Tg elastomers, however, have poor compatibility with the hydrocarbon-based plasticizing resins typically used in tires, rendering them unsuitable for easy and optimal use in compositions for tires which may have the best compromise between performance properties that are difficult to reconcile simultaneously (namely wear resistance and grip, which must be high, and rolling resistance, which must be low in order to minimize fuel consumption).

Thus, it is currently beneficial for tire manufacturers to find formulas which make it possible to improve the balance between all of these performance properties, especially by improving the compatibility of the elastomers with the hydrocarbon-based plasticizing resins.

Document WO2013/176712 describes various resins of cyclopentadiene/dicyclopentadiene/methylcyclopentadiene type, having specific weights and softening points. In this document, these resins are used in the disclosed examples to improve wet grip.

Documents WO2017/064235 and WO2017/168099 also describe various resins of cyclopentadiene/dicyclopentadiene/methylcyclopentadiene type, and their use in tires having improved having high grip and low rolling resistance.

At present, the Applicants have shown that a particular composition comprising a specific hydrocarbon-based resin makes it possible to obtain tires with improved road behavior at various temperatures. The invention relates to such tires, as further describes below.

SUMMARY

Described herein are tires comprising a rubber composition based on at least an elastomer and a hydrocarbon resin, wherein said hydrocarbon resin is based on a cyclic monomer selected from the group consisting of a distillation cut from a petroleum refinery stream, and/or C₄, C₅ or C₆ cyclic olefins and mixtures thereof, and wherein the hydrocarbon resin has a number average molecular weight (Mn) of between 150 and 800 g/mol, and a content of aromatic protons (H Ar, expressed in mol %), a glass transition temperature (Tg, is expressed in ° C.), and a number average molecular weight (Mn, expressed in g/mol) that are represented by (1) H Ar ≤ 6 mol %, (2) Tg ≥ 95 - 2.2*(H Ar), (3) Tg ≥ 125 - (0.08*Mn).

The tire according to the invention will be chosen from, without limitation, the tires intended to equip a two-wheeled vehicle, a passenger vehicle, or else a "heavy-duty" vehicle (that is to say, underground train, bus, off-road vehicles, heavy road transport vehicles, such as lorries, tractors or trailers), or else aircraft, construction equipment, heavy agricultural vehicles or handling vehicles

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is graph of the Tg and H Ar relationship of the present hydrocarbon resin, comparative resin and prior art elastomeric compositions.

FIG. 2 is a graph of Tg and M_n relationship of the present hydrocarbon resins, comparative prior art hydrocarbon additives and prior art comparative elastomeric compositions.

DETAILED DESCRIPTION OF THE INVENTION

Provided herein are tires comprising a rubber composition based on at least an elastomer and a hydrocarbon resin, wherein said hydrocarbon resin is based on a cyclic monomer selected from the group consisting of a distillation cut from a petroleum refinery stream, and/or C₄, C₅ or C₆ cyclic olefins and mixtures thereof, and wherein the hydrocarbon resin has a number average molecular weight (Mn) of between 150 and 800 g/mol, and a content of aromatic protons (H Ar, expressed in mol %), a glass transition temperature (Tg, is expressed in ° C.), and a number average molecular weight (Mn, expressed in g/mol) that are represented by (1) H Ar ≤ 6 mol %, (2) Tg ≥ 95 - 2.2*(H Ar), (3) Tg ≥ 125 - (0.08*Mn).

Definitions

For the purposes of this disclosure, the following definitions will apply, unless otherwise stated:

As used herein, the singular form of "a," "an," and "the" include plural referents unless otherwise specified.

The term "predominant compound" refers to a compound that is predominant among the compounds of the same type in a composition. For example, the predominant compound is one that represents the greatest amount by weight among the compounds of the same type in a composition. Thus, for example, a predominant polymer is the polymer representing the greatest weight relative to the total weight of the polymers in the composition.

The term, "predominant unit" refers to a unit within the same compound (or polymer) that is predominant among the units forming the compound (or polymer) and which represents the greatest fraction by weight among the units forming the compound (or polymer). For example, the hydrocarbon resin can comprise predominant units of cyclopentadiene where the cyclopentadiene units represent the greatest amount by weight among all the units comprising the resin. Similarly, as described herein, the hydrocarbon resin can comprise predominant units selected from the group of cyclopentadiene, dicyclopentadiene, methylcyclopentadiene and mixtures thereof where the sum of the units selected from the group of cyclopentadiene, dicyclopentadiene, methylcyclopentadiene and the mixtures thereof represents the greatest number by weight among all of the units.

The term, a "predominant monomer" refers to a monomer which represents the greatest fraction by weight in the total polymer. Conversely, a "minor" monomer is a monomer which does not represent the greatest molar fraction in the polymer.

The phrase "composition based on" refers to a composition comprising the mixture and/or the product of the in situ reaction of the various base constituents used, some of these constituents being able to react and/or being intended to react with one another, at least partially, during the various phases of manufacture of the composition or during the subsequent curing, which may modify the composition as it is prepared at the start. Thus, compositions described below can be different in the non-crosslinked state and in the crosslinked state.

Unless expressly indicated otherwise, all the percentages (%) shown are percentages by weight ("wt. %"). Further-

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more, any range of values denoted by the expression “between a and b” represents the range of values extending from more than a to less than b (that is to say, limits a and b excluded), while any range of values denoted by the expression “from a to b” means the range of values extending from a up to b (that is to say, including the strict limits a and b).

Rubber Compositions

The tire of the invention comprises a rubber composition based on at least an elastomer and a specific hydrocarbon resin, as described below. Said rubber composition may also comprise various optional ingredients, well known by the person skilled in the art. Some of them are also described below.

Hydrocarbon Resin

The hydrocarbon resin is based on a cyclic monomer selected from the group consisting of a distillation cut from a petroleum refinery stream, and/or C_4 , C_5 or C_6 cyclic olefins and mixtures thereof, and wherein the hydrocarbon resin has a number average molecular weight (M_n) of between 150 and 800 g/mol, and a content of aromatic protons (H Ar, expressed in mol %), a glass transition temperature (T_g , is expressed in °C.), and a number average molecular weight (M_n , expressed in g/mol) that are represented by (1) $H\ Ar \leq 6$ mol %, (2) $T_g \geq 95 - 2.2 * (H\ Ar)$, (3) $T_g \geq 125 - (0.08 * M_n)$.

The phrase “hydrocarbon resin based on” refers to the polymer resulting from the polymerization of the proposed monomers, i.e.: cyclic monomers and/or aromatic monomers, such monomers after the polymerization reaction being changed to their corresponding units in the polymer. Such polymerization of cyclic monomers and/or aromatic monomers would result in hydrocarbon resins comprising the corresponding cyclic units and/or aromatic units.

As used herein, the term, “cyclic monomer” refers to a distillation cut and/or synthetic mixture of C_5 and C_6 cyclic olefins, diolefins, dimers, codimers, and trimers. More specifically, cyclic monomers include, but are not limited to, cyclopentene, cyclopentadiene (“CPD”), dicyclopentadiene (“DCPD”), cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, methylcyclopentadiene (“MCPD”), di(methylcyclopentadiene) (“MCPD dimer”), and codimers of CPD and/or MCPD with C_4 cyclics such as butadienes, C_5 cyclics such as piperylene. An exemplary cyclic monomer is cyclopentadiene. Optionally, the cyclic monomers can be substituted. The dicyclopentadiene can be in either the endo or exo form.

Substituted cyclic monomers include cyclopentadienes and dicyclopentadienes substituted with a C_1 to C_{40} linear, branched, or cyclic alkyl group. In an aspect the substituted cyclic monomer can have one or more methyl groups. In an aspect, the cyclic monomers are selected from the group of: cyclopentadiene, cyclopentadiene dimer, cyclopentadiene- C_4 codimer, cyclopentadiene- C_5 codimer, cyclopentadiene-methylcyclopentadiene codimer, methylcyclopentadiene- C_4 codimer, methylcyclopentadiene- C_5 codimer, methylcyclopentadiene dimer, cyclopentadiene and methylcyclopentadiene trimers and cotrimers, and/or mixtures thereof.

In an aspect, the cyclic monomer is selected in the group consisting of cyclopentene, cyclopentadiene, dicyclopentadiene, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, methylcyclopentadiene, di(methylcyclopentadiene) and mixtures thereof. In an aspect, the cyclic monomer is

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selected from the group of dicyclopentadiene, cyclopentadiene, and methylcyclopentadiene. In an aspect, the cyclic monomer is cyclopentadiene.

In an aspect, the hydrocarbon resin comprises the cyclic monomer in an amount between 20 wt. % and 99 wt. %. In an aspect, the hydrocarbon resin comprises the cyclic monomer in an amount between 25 wt. % and 80 wt. %. In an aspect, the hydrocarbon resin comprises the cyclic monomer in an amount between 40 wt. % and 75 wt. %.

In an aspect, the hydrocarbon resin comprises dicyclopentadiene, cyclopentadiene, and/or methylcyclopentadiene in an amount between 20 wt. % and 99 wt. %, and in a more specific aspect, in an amount between 25 wt. % and 80 wt. %. In an aspect, the hydrocarbon resin comprises dicyclopentadiene, cyclopentadiene, and/or methylcyclopentadiene in an amount between 40 wt. % and 75 wt. %. In an aspect, the hydrocarbon resin comprises methylcyclopentadiene in an amount between 0.1 wt. % and 15 wt. %. In an aspect, the hydrocarbon resin comprises methylcyclopentadiene in an amount between 0.1 wt. % and 5 wt. %.

The subject hydrocarbon resin comprises one or more cyclic monomers that are used to prepare one or more complex copolymers as described herein. The makeup of the complex copolymer can be controlled by the type and the amount of monomer included in the resin, i.e., the microstructure of the copolymer. Monomer placement in the polymer chain, however, is random, leading to further complexity in the polymer microstructure.

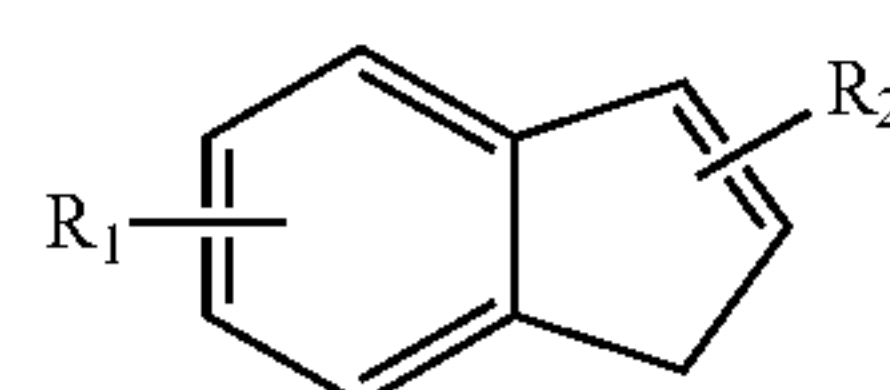
In an aspect, the hydrocarbon resin further comprises an aromatic monomer. In an aspect, the aromatic monomer is selected in the group consisting of an olefin-aromatic compounds, aromatic distillation cuts and mixtures thereof.

In an aspect, the hydrocarbon resin comprises the aromatic monomer in an amount between 1 wt. % and 40 wt. %. In an aspect, the hydrocarbon resin comprises the aromatic monomer in an amount between 10 wt. % and 30 wt. %.

In an aspect, the aromatic monomer is an aromatic distillation cut. In an aspect, the hydrocarbon resin comprises an aromatic distillation cut from a petroleum refinery stream such as one obtained by steam cracking streams and then separating the fraction boiling in the range of 135° C. to 220° C. by fractional distillation. In an aspect, the aromatic distillation cut component comprises at least one of styrene, alkyl substituted derivatives of styrene, indene, alkyl substituted derivatives of indene or mixtures thereof. In an aspect, the aromatic distillation cut component comprises 4 wt. % to 7 wt. % of styrene; 20 wt. % to 30 wt. % of alkyl substituted derivatives of styrene, 10 wt. % to 25 wt. % indene, 5 to 10 wt. % alkyl substituted derivatives of indene and 35 wt. % to 45 wt. % non-reactive aromatics.

In an aspect, the aromatic monomer comprises an olefin-aromatic compound selected from the group consisting of indene derivatives, vinylaromatic compounds and mixtures thereof.

In an aspect, the aromatic monomer comprises an indene derivative represented by Formula (I):



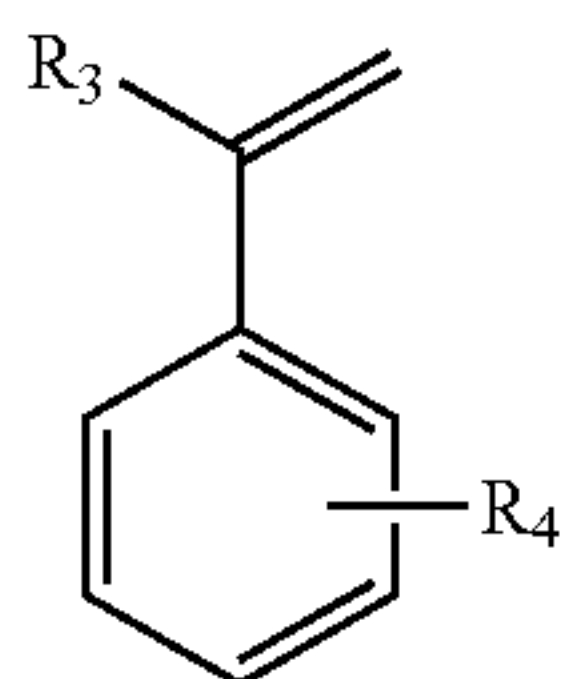
(I)

wherein R_1 and R_2 represent, independently of one another, a hydrogen atom, an alkyl group, an alkenyl group, a

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cycloalkyl group, an aryl group or an arylalkyl group. For example such compounds can be 1H-Indene; 1-methyl-1H-indene; alkyl Indene; 5-(2-methylbut-2-enyl)-1H-indene; 5,6,7,8-tetrahydro-1H-cyclopentanaphthalene; 4HIndene-5butan-1 ol or derivatives thereof.

In an aspect, the aromatic monomer comprises a vinylaromatic compound represented by Formula (II)



wherein R_3 and R_4 represent, independently of one another, a hydrogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group or an arylalkyl group. Alpha-methylstyrene or substituted alpha-methylstyrenes having one or more substituents on the aromatic ring are suitable, particularly where the substituents are selected from alkyl, cycloalkyl, aryl, or combination radicals, each having one to eight carbon atoms per substituent. Non-limiting examples include alpha-methyl styrene, alpha-methyl-4-butyl styrene, alpha-methyl-3,5-di-t-bensystyrene, alpha-methyl-3,4,5-trimethyl styrene, alpha-methyl-4-benzylstyrene, alpha-methyl-4-chlorohexylstyrene, and/or mixtures thereof.

The present hydrocarbon resins can be prepared using different methodologies. For example, thermal polymerization of cyclic feed streams can be used in combination or absence of olefin-aromatics, substituted benzene and aromatic distillation cut. As described in the Examples below, different resins were prepared to achieve a desired molecular weight and a certain tackifier cloud point. Specifically, Tables 2A, 2B, 3A and 3B below describe the feed streams, polymerization conditions and final properties of the present hydrocarbon resins.

Incompatibility with base polymers can limit the applications for resins having high Tg where low molecular weight and ease of processing is desirable. The present hydrocarbon resins overcome this deficiency with the novel combination of the Tg and Mn not previously described.

Specifically, the hydrocarbon resin hydrocarbon resin has a content of aromatic proton ("H Ar"), as expressed in percent, of less than or equal to 6 mole %. Further, the hydrocarbon resins are defined by the glass transition temperature ("Tg") and aromatic proton content ("H Ar") as well as the glass transition temperature ("Tg") and number average molecular weight ("Mn"). Even more specifically the present hydrocarbon resins are defined as: $Tg \geq 95 - 2.2 * (H\ Ar)$; and $Tg \geq 125 - (0.08 * Mn)$, where Tg is glass transition temperature expressed in ° C. of the resin, H Ar represents the content of aromatic protons in the resin and Mn represents the number average molecular weight of the resin.

In an aspect, the hydrocarbon resin has at least one and preferably all of the following additional features:

- a MMAP cloud point of between 10° C. and 60° C.,
- a number average molecular weight (Mn) of between 250 and 600 g/mol,
- a glass transition temperature (Tg) of 95° C. or more,
- a content of aromatic protons (H Ar) 3 mol % or less.

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As described above, the present rubber compositions comprise one or more of the present hydrocarbon resins.

The content of the hydrocarbon resin in the rubber composition can be within a range extending from 15 phr to 150 phr, from 25 phr to 120 phr, from 40 phr to 115 phr, from 50 phr to 110 phr, and from 65 phr to 110 phr. Below 15 phr of the present hydrocarbon resin, the effect of the present hydrocarbon resin becomes insufficient and the rubber composition could have problems of grip. Above 150 phr, the composition could present manufacturing difficulties in terms of readily incorporating the present hydrocarbon resin into the composition.

Elastomer

The tire of the invention comprises a rubber composition based on at least an elastomer and a specific hydrocarbon resin as described above. The elastomer will be further described below.

As used herein, the terms "elastomer" and "rubber" are used interchangeably. They are well known by the person skilled in the art.

"Diene elastomer" refers to an elastomer resulting at least in part (homopolymer or copolymer) from diene monomers (monomers bearing two double carbon-carbon bonds, whether conjugated or not). The diene elastomer can be "highly unsaturated," resulting from conjugated diene monomers, which have a greater than 50% molar content of units.

Diene elastomers can be classified into two categories: "essentially unsaturated" or "essentially saturated". "Essentially unsaturated" is understood to mean generally a diene elastomer resulting at least in part from conjugated diene monomers having a content of units of diene origin (conjugated dienes) which is greater than 15% (mol %); thus, diene elastomers such as butyl rubbers or copolymers of dienes and of α -olefins of EPDM type do not fall under the preceding definition and may especially be described as "essentially saturated" diene elastomers (low or very low content, always less than 15%, of units of diene origin). In the category of "essentially unsaturated" diene elastomers, "highly unsaturated" diene elastomer is understood in particular to mean a diene elastomer having a content of units of diene origin (conjugated dienes) which is greater than 50%.

Given the definitions provided above, diene elastomer refers to:

- (a) any homopolymer obtained by polymerization of a conjugated diene monomer having from 4 to 12 carbon atoms;
- (b) any copolymer obtained by copolymerization of one or more conjugated dienes with one another or with one or more vinylaromatic compounds having from 8 to 20 carbon atoms;
- (c) a ternary copolymer obtained by copolymerization of ethylene and of an α -olefin having from 3 to 6 carbon atoms with a non-conjugated diene monomer having from 6 to 12 carbon atoms, such as, for example, the elastomers obtained from ethylene and propylene with a non-conjugated diene monomer of the abovementioned type, such as, especially, 1,4-hexadiene, ethylidene norbornene or dicyclopentadiene;
- (d) a copolymer of isobutene and of isoprene (butyl rubber) and also the halogenated versions, in particular chlorinated or brominated versions, of this type of copolymer.

Although it applies to any type of diene elastomer, essentially unsaturated diene elastomers, in particular of type (a) or (b) above can be useful in tire applications.

The following are especially suitable as conjugated dienes: 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C₁-C₅ alkyl)-1,3-butadienes, such as, for example, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, aryl-1,3-butadiene, 1,3-pentadiene or 2,4-hexadiene. The following, for example, are suitable as vinylaromatic compounds: styrene, ortho-, meta- or para-methylstyrene, the "vinyltoluene" commercial mixture, para-(tert-butyl)styrene, methoxystyrenes, chlorostyrenes, vinylmesitylene, divinylbenzene or vinylnaphthalene.

The copolymers may contain between 99% and 20% by weight of diene units and between 1% and 80% by weight of vinylaromatic units. The elastomers can have any microstructure, which depends on the polymerization conditions used, especially on the presence or absence of a modifying and/or randomizing agent and on the amounts of modifying and/or randomizing agent employed. The elastomers can, for example, be block, random, sequential or microsequential elastomers and can be prepared in dispersion or in solution; they can be coupled and/or star-branched or else functionalized with a coupling and/or star-branching or functionalization agent. "Function" here is preferentially understood to mean a chemical group which interacts with the reinforcing filler of the composition.

To summarize, the diene elastomer of the composition is preferentially selected from the group of highly unsaturated diene elastomers consisting of polybutadienes (abbreviated to "BRs"), synthetic polyisoprenes (IRs), natural rubber (NR), butadiene copolymers, isoprene copolymers and the mixtures of these elastomers. Such copolymers are more preferentially selected from the group consisting of butadiene/styrene (SBR) copolymers.

Thus, the invention preferably relates to compositions in which the elastomer said diene elastomer is selected from the group consisting of essentially unsaturated diene elastomers, and especially from the group consisting of polybutadienes, synthetic polyisoprenes, natural rubber, butadiene copolymers, isoprene copolymers and the mixtures of these elastomers.

According to a particularly preferred mode of the invention, the elastomer predominantly comprises an elastomer, preferentially a diene elastomer, having a glass transition temperature T_g of less than -40° C., preferably of between -40° C. and -110° C., more preferably between -60° C. and -110° C., more preferably between -80 and -110° C. and even more preferably between -90° C. and -110° C.

Preferably, the predominant diene elastomer is selected from the group consisting of polybutadienes, butadiene copolymers and mixtures of these elastomers, and more preferentially from the group consisting of polybutadienes, copolymers of butadiene and styrene, and the mixtures of these elastomers.

According to this embodiment, the predominant, preferentially diene, elastomer having a very low T_g is present in the composition at a content preferentially greater than or equal to 60 phr, more preferentially greater than or equal to 70 phr and more preferentially still greater than or equal to 80 phr. More preferably, the composition comprises 100 phr of elastomer having a very low T_g as defined above.

Reinforcing Filler

The composition can comprise a reinforcing filler. Use may be made of any type of reinforcing filler known for its

abilities to reinforce a rubber composition which can be used for the manufacture of tires, for example an organic filler, such as carbon black, a reinforcing inorganic filler, such as silica or alumina, or also a blend of these two types of filler.

As described herein, reinforcing filler can be selected from the group consisting of silicas, carbon blacks and the mixtures thereof.

The content of reinforcing filler can be within a range extending from 5 phr to 200 phr, and from 40 to 160 phr. In an aspect, reinforcing filler is silica, in an aspect, at a content within a range extending from 40 phr to 150 phr. The composition provided herein can comprise a minority amount of carbon black, where, in an aspect, the content is within a range extending from 0.1 phr to 10 phr.

All carbon blacks, especially "tyre-grade" blacks, are suitable as carbon blacks. Mention will more particularly be made, among the latter, of the reinforcing carbon blacks of the 100, 200 or 300 series (ASTM grades), such as, for example, the N115, N134, N234, N326, N330, N339, N347 or N375 blacks, or else, depending on the applications targeted, the blacks of higher series (for example N660, N683 or N772). The carbon blacks might, for example, be already incorporated in an isoprene elastomer in the form of a masterbatch (see, for example, Applications WO 97/36724 or WO 99/16600).

The present rubber compositions can comprise one type of silica or a blend of several silicas. The silica used can be any reinforcing silica, especially any precipitated or fumed silica exhibiting a BET surface area and a CTAB specific surface area, each one being less than 450 m²/g, such as from 30 m²/g to 400 m²/g. Mention will be made, as highly dispersible precipitated silicas ("HDSs"), for example, of the "Ultrasil 7000" and "Ultrasil 7005" silicas from Degussa, the "Zeosil 1165MP", "1135MP" and "1115MP" silicas from Rhodia, the "Hi-Sil EZ150G" silica from PPG, the "Zeopol 8715", "8745" and "8755" silicas from Huber, treated precipitated silicas, such as, for example, the silicas "doped" with aluminium described in Application EP-A-0735088, or the silicas with a high specific surface as described in Application WO 03/16837. The silica can have a BET specific surface of between 45 and 400 m²/g, and preferably between 60 and 300 m²/g.

The present rubber compositions can optionally also comprise (in addition to the coupling agents) coupling activators, agents for covering the inorganic fillers and any other processing aid capable by virtue of an improvement in the dispersion of the filler in the rubber matrix and of a lowering of the viscosity of the compositions, of improving their ability to be processed in the raw state, these agents being, for example, hydrolysable silanes, such as alkylalkoxysilanes, polyols, fatty acids, polyethers, primary, secondary or tertiary amines, or hydroxylated or hydrolysable polyorganosiloxanes.

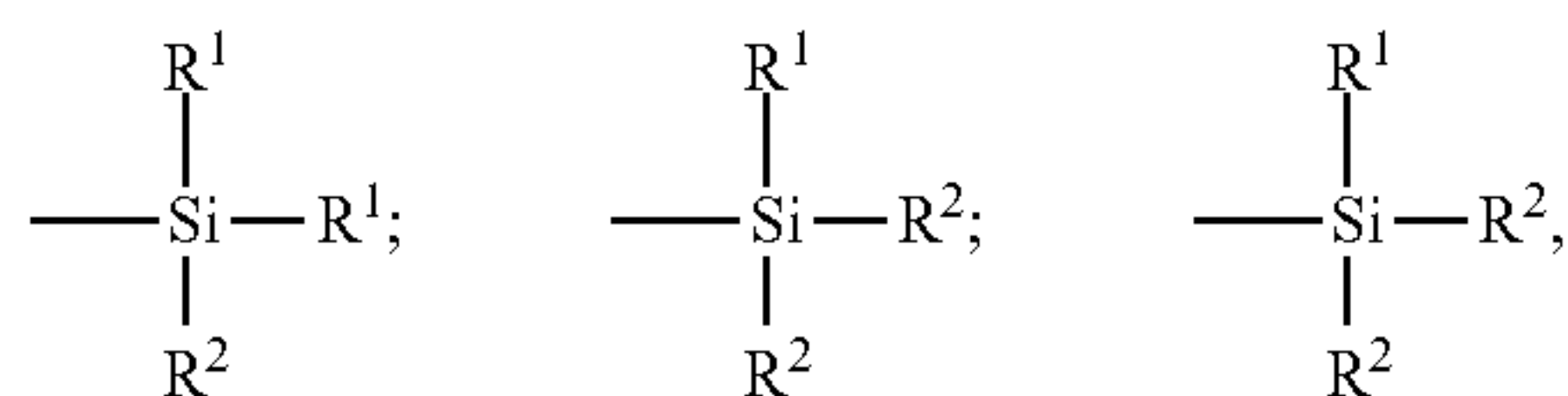
Use can be made especially of silane polysulfides, referred to as "symmetrical" or "asymmetrical" depending on their specific structure, such as described, for example, in applications WO 03/002648 (or US 2005/016651) and WO 03/002649 (or US 2005/016650).

Also, suitable in particular, without the definition below being limiting, are silane polysulfides referred to as "symmetrical," corresponding to the following general Formula III: (III) Z-A-S_x-A-Z, in which:

x is an integer from 2 to 8 (such as from 2 to 5);

A is a divalent hydrocarbon radical (such as C₁-C₁₈ alkylene groups or C₆-C₁₂ arylene groups, more particularly C₁-C₁₀ alkylenes, in particular C₁-C₄ alkylenes, especially propylene);

Z corresponds to one of the formulae below:



in which:

the R¹ radicals, which are substituted or unsubstituted and identical to or different from one another, represent a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkyl or C₆-C₁₈ aryl group (as such C₁-C₆ alkyl, cyclohexyl or phenyl groups, in particular C₁-C₄ alkyl groups, more particularly methyl and/or ethyl),

the R² radicals, which are substituted or unsubstituted and identical to or different from one another, represent a C₁-C₁₈ alkoxy or C₅-C₁₈ cycloalkoxy group (such as a group chosen from C₁-C₈ alkoxys and C₅-C₈ cycloalkoxys, such as a group chosen from C₁-C₄ alkoxys, in particular methoxy and ethoxy).

In the case of a mixture of alkoxysilane polysulfides corresponding to the above Formula (III), especially normal commercially available mixtures, the mean value of the “x” indices is a fractional number such as between 2 and 5, of approximately 4. However, advantageously, the mixture can be carried out with alkoxysilane disulfides (x=2). Examples include silane polysulfides of bis((C₁-C₄)alkoxy(C₁-C₄)alkylsilyl(C₁-C₄)alkyl) polysulfides (especially disulfides, trisulfides or tetrasulfides), such as, for example, bis(3-trimethoxysilylpropyl) or bis(3-triethoxysilylpropyl) polysulfides. Use can be made in particular, among these compounds, of bis(3-triethoxysilylpropyl) tetrasulfide, abbreviated to TESPT, of formula [(C₂H₅O)₃Si(CH₂)₃S₂]₂, or bis(3-triethoxysilylpropyl) disulfide, abbreviated to TESP, of formula [(C₂H₅O)₃Si(CH₂)₃S]₂. Other examples include bis(mono(C₁-C₄)alkoxydi(C₁-C₄)alkylsilylpropyl) polysulfides (in particular disulfides, trisulfides or tetrasulfides), more particularly bis(monoethoxydimethylsilylpropyl) tetrasulfide, such as described in Patent Application WO 02/083782 (or US 2004/132880). Mention will also be made, as coupling agent other than alkoxysilane polysulfide, of bifunctional POSSs (polyorganosiloxanes) or else of hydroxysilane polysulfides (R²=OH in the above formula III), such as described in published patent applications WO 02/30939 (or U.S. Pat. No. 6,774,255) and WO 02/31041 (or US 2004/051210), or else of silanes or POSSs bearing azodicarbonyl functional groups, such as described, for example, in published patent applications WO 2006/125532, WO 2006/125533 and WO 2006/125534.

The content of coupling agent in the present compositions can be between 1 phr to 15 phr, and between 3 phr to 14 phr.

In addition, filler can be made of a reinforcing filler of another nature, especially organic, provided that this reinforcing filler is covered with a layer of silica or else comprises functional sites, especially hydroxyl sites, at its surface which require the use of a coupling agent in order to form the bond between the filler and the elastomer.

The physical state in which the reinforcing filler is provided is not important, whether it is in the form of a powder, micropearl, granule, bead and/or any other appropriate densified form.

Crosslinking Systems

In the rubber compositions provided herein, any type of crosslinking system for rubber compositions can be used.

The crosslinking system can be a vulcanization system, that is to say based on sulfur (or on a sulfur-donating agent) and a primary vulcanization accelerator. Various known secondary vulcanization accelerators or vulcanization activators, such as zinc oxide, stearic acid or equivalent compounds, or guanidine derivatives (in particular diphenylguanidine), may be added to this base vulcanization system, being incorporated during the first non-productive phase and/or during the productive phase, as described subsequently.

Sulfur can be used at a content of between 0.5 phr and 10 phr, between 0.5 phr and 5 phr, in particular between 0.5 and 3 phr.

The vulcanization system of the composition also can comprise one or more additional accelerators, for example compounds of the family of the thiurams, zinc dithiocarbamate derivatives, sulfenamides, guanidines or thiophosphates. Use may in particular be made of any compound capable of acting as accelerator of the vulcanization of diene elastomers in the presence of sulfur, especially accelerators of thiazoles type and also their derivatives, accelerators of the thiurams type, and zinc dithiocarbamates. These accelerators are selected from the group consisting of 2-mercaptobenzothiazole disulfide (abbreviated to “MBTS”), N-cyclohexyl-2-benzothiazolesulfenamide (abbreviated to “CBS”), N,N-dicyclohexyl-2-benzothiazolesulfenamide (abbreviated to “DCBS”), N-(tert-butyl)-2-benzothiazolesulfenamide (abbreviated to “TBBS”), N-(tert-butyl)-2-benzothiazolesulfenimide (abbreviated to “TBSI”), zinc dibenzylthiocarbamate (abbreviated to “ZBEC”) and the mixtures of these compounds. Use is made of a primary accelerator of the sulfenamide type.

The rubber compositions can optionally comprise all or a portion of the normal additives customarily used in elastomer compositions intended especially for the manufacture of treads, such as, for example, pigments, protective agents, such as antiozone waxes, chemical antiozonants or antioxidants, plasticizing agents other than those described above, anti-fatigue agents, reinforcing resins, or methylene acceptors (for example, novolac phenolic resin) or donors (for example HMT or H3M).

The rubber compositions can also comprise a plasticizing system. This plasticizing system may be composed of a hydrocarbon-based resin with a Tg of greater than 20° C., in addition to the specific hydrocarbon-based resin described above, and/or a plasticizing oil.

Of course, the compositions can be used alone or in a blend (i.e., in a mixture) with any other rubber composition which can be used in the manufacture of tires.

The rubber compositions described herein can be both in the “uncured” or non-crosslinked state (i.e., before curing) and in the “cured” or crosslinked, or else vulcanized, state (i.e., after crosslinking or vulcanization).

Preparation of the Rubber Compositions

The rubber compositions are manufactured in appropriate mixers, using two successive phases of preparation: a first phase of thermomechanical working or kneading (sometimes referred to as “non-productive” phase) at high temperature, up to a maximum temperature of between 110° C. and 200° C., for example between 130° C. and 180° C., followed by a second phase of mechanical working (sometimes referred to as “productive” phase) at lower temperature, typically below 110° C., for example between 60° C. and 100° C., during which finishing phase the crosslinking or vulcanization system is incorporated; such phases have

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been described, for example, in applications EP-A-0 501 227, EP-A-0 735 088, EP-A-0 810 258, WO 00/05300 or WO 00/05301.

The first (non-productive) phase is carried out in several thermomechanical stages. During a first step, the elastomers, the reinforcing fillers and the hydrocarbon resin (and optionally the coupling agents and/or other ingredients, with the exception of the crosslinking system) are introduced into an appropriate mixer, such as a customary internal mixer, at a temperature between 20° C. and 100° C. and, preferably between 25° C. and 100° C. After a few minutes, from 0.5 to 2 min, and a rise in the temperature to 90° C. or to 100° C., the other ingredients (that is to say, those which remain, if not all were put in at the start) are added all at once or in portions, with the exception of the crosslinking system, during a mixing ranging from 20 seconds to a few minutes. The total duration of the kneading, in this non-productive phase, is between 2 and 10 minutes at a temperature of less than or equal to 180° C. and preferably less than or equal to 170° C.

After cooling the mixture thus obtained, the crosslinking system is then incorporated at low temperature (typically less than 100° C.), generally in an external mixer, such as an open mill. The combined mixture is then mixed (productive phase) for several minutes, for example between 5 and 15 min.

The final composition thus obtained is subsequently calendered, for example in the form of a sheet or slab, in particular for laboratory characterization, or else extruded, in order to form, for example, a rubber profiled element used in the manufacture of semi-finished products for tires. These products may then be used for the manufacture of tires, with the advantage of having good tack of the layers on one another before curing of the tire.

The crosslinking (or curing) can be carried out at a temperature generally of between 130° C. and 200° C., under pressure, for a sufficient time which can vary, for example, between 5 and 90 min, as a function in particular of the curing temperature, of the crosslinking system adopted, of the kinetics of crosslinking of the composition under consideration or else of the size of the tire.

Test Methods Useful for Invention

The features of the present hydrocarbon resins and compositions containing the hydrocarbon resin are demonstrated in the following non-limiting examples. Test methods and experimental procedures used in the examples are described immediately below.

Molecular weight distribution ("MWD") is equivalent to the expression M_w/M_n . The expression M_w/M_n the ratio of the weight average molecular weight (M_w) to the number average molecular weight (M_n).

The weight average molecular weight is given by

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

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the number average molecular weight is given by

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

the z-average molecular weight is given by

$$M_z = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2}$$

where n_i in the foregoing equations is the number fraction of molecules of molecular weight M_i . Measurements of M_w , M_z , and M_n are determined by Gel Permeation Chromatography as described further below.

Gel Permeation Chromatography (GPC). The distribution and the moments of molecular weight (M_w , M_n , M_w/M_n , etc.) were determined by using room temperature (20° C.) Gel Permeation Chromatography equipped using "Tosoh EcoSEC HLC-8320GPC" with enclosed Refractive Index (RI) Ultraviolet and (UV) detectors. Four "Agilent PLgel" of 5 μ m 50 Å; 5 μ m 500 Å; 5 μ m 10E3 Å; 5 μ m Mixed-D were used in series. "Aldrich" reagent grade tetrahydrofuran (THF) was used as the mobile phase. The polymer mixture was filtered through a 0.45 μ "Teflon" filter and degassed with an online degasser before entering the GPC instrument. The nominal flow rate was 1.0 mL/min and the nominal injection volume is 200 μ L. The molecular weight analysis was performed with "EcoSEC" software.

The concentration (c), at each point in the chromatogram was calculated from the baseline-subtracted IRS broadband signal intensity (I), using the following equation: $c = \beta I$, where " β " is the mass constant determined with polystyrene standards. The mass recovery was calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume.

Molecular Weight. The molecular weight was determined by using a polystyrene calibration relationship with the column calibration which is performed with a series of mono-dispersed polystyrene (PS) standards of 162, 370, 580, 935, 1860, 2980, 4900, 6940, 9960, 18340, 30230, 47190 & 66000 kg/mole. The molecular weight "M" at each elution volume is calculated with following equation:

$$\log M = \frac{\log(K_{PS}/K)}{a+1} + \frac{a_{PS}+1}{a+1} \log M_{PS}$$

where the variables with subscript "PS" stand for polystyrene while those without a subscript correspond to the test samples. In this method $a_{PS}=0.67$ and $K_{PS}=0.000175$, "a" and "K" being calculated from a series of empirical formula (T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, 34(19) MACROMOLECULES 6812-6820 (2001)). Specifically, $a/K=0.695/0.000579$ for polyethylene and $0.705/0.0002288$ for polypropylene. All concentrations are expressed in g/cm³, molecular weight is expressed in g/mole, and intrinsic viscosity is expressed in dL/g unless otherwise noted.

DSC Measurements. The following DSC procedure was used to determine the glass transition temperatures (T_g) of hydrocarbon resin. Approximately 6 mg of material was placed in a microliter aluminum sample pan. The sample was placed in a differential scanning calorimeter ("Perkin Elmer" or "TA Instrument" Thermal Analysis System) and was heated from 23° C. to 200° C. at 10° C./minute and held at 200° C. for 3 minutes. Afterward, the sample was cooled down to -50° C. at 10° C./minute. The sample was held at -50° C. for 3 minutes and then heated from -50° C. to 200° C. at 10° C./minute for a second heating cycle. The T_g was determined in the "TA Universal Analysis" on the second heating cycle, using inflection method. The "Glass Transition" menu item on the "TA Universal Analysis" equipment is used to calculate the onset, end, inflection, and signal change of T_g in the DSC. The program enables the determination of the onset, which is the intersection of the first and second tangents, where the inflection is the portion of the curve between the first and third tangents with the steepest slope, and the end is the intersection of the second and third tangents. The T_g of the hydrocarbon resin is the inflection temperature of the curve.

Aromatic Protons (H AR) percentage: 500 MHz NMR instrument is used, in TCE-d₂(1, 2 dichloroethane) or CDC13 (chloroform) solvent at 25° C. and 120 scans are done. NMR data of the hydrocarbon resin were measured by dissolving 20±1 mg of sample in 0.7 ml of d-solvents. The samples are dissolved in TCE-d₂ in 5 mm NMR tube at 25° C. until the sample was dissolved. There is no standard used. The TCE-d₂/CDC13 presents as a peak at 5.98 or 7.24 ppm and used as the reference peak for the samples. The ¹H NMR signals of the aromatic protons are located between 8.5 ppm and 6.2 ppm. The ethylenic protons give rise to signals between 6.2 ppm and 4.5 ppm. Finally, the signals corresponding to aliphatic protons are located between 4.5 ppm and 0 ppm. The areas of each category of protons are related to the sum of these areas to thereby give a distribution in terms of % of area for each category of protons.

MMA Cloud Point. MMA cloud point is the temperature where one or more modifiers, tackifiers or agents as dissolved in solvent is no longer completely soluble (as determined by a cloudy appearance of the tackifier/solvent mixture). As presented herein, MMA cloud points were determined using a modified ASTM D-611-82 method, substituting methylcyclohexane for the heptane used in the standard test procedure. The procedure used tackifier/aniline/methylcyclohexane in a ratio of 1/2/1 (5 g/10 mL/5 mL). The MMA cloud point was determined by cooling a heated, clear blend of the three components until a complete turbidity occurs.

Softening Point. "Softening Point" is the temperature, measured in ° C., at which a material will flow, as determined according to the Ring & Ball Method, as measured by ASTM E-28. As a rule of thumb, the relationship between T_g and softening point is approximately: T_g=softening point -50° C.

Dynamic Properties of Compositions (After Curing)

The dynamic properties G* and tan(δ)_{max} are measured on a viscosity analyzer ("MetraVib V A4000") according to Standard ASTM D 5992-96. The response of a sample of vulcanized composition (cylindrical test specimen with a thickness of 4 mm and a diameter of 10 mm), subjected to a simple alternating sinusoidal shear stress, at a frequency of 10 Hz, under temperature condition (23° C.) according to Standard ASTM D 1349-99, or at a different temperature. A

deformation sweep is performed from 0.1% to 50% (forward cycle), then from 50% to 0.1% (return cycle). For the return cycle, the value of rigidity at 10% deformation is then noted.

The higher the value of rigidity at 10% deformation and 23° C., the more the composition will provide good road handling. The results are expressed in terms of performance base 100, that is to say that the value 100 is arbitrarily assigned to the control, in order to subsequently compare the G*10% at 23° C. (that is to say the rigidity and hence the road handling) of the various solutions tested. The value in base 100 is calculated according to the operation (value of G*10% at 23° C. of the sample/value of G*10% at 23° C. of the control)*100. Therefore, a higher value represents an improvement of the road handling performance, while a lower value represents a reduction in the road handling performance.

The higher the value of rigidity at 10% deformation and 40° C., the more the composition will provide good road handling. The results are expressed in terms of performance base 100, that is to say that the value 100 is arbitrarily assigned to the control, in order to subsequently compare the G*10% at 40° C. (that is to say the rigidity and hence the road handling) of the various solutions tested. The value in base 100 is calculated according to the operation (value of G*10% at 40° C. of the sample/value of G*10% at 40° C. of the control)*100. Therefore, a higher value represents an improvement of the road handling performance, while a lower value represents a reduction in the road handling performance.

The following examples are intended to highlight various aspects of certain embodiments of the present invention. It should be understood, however, that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention, unless otherwise specifically indicated.

Example 1

With respect to processes for making prior art hydrocarbon resins, they have been prepared by thermally polymerizing a mixture consisting essentially of 5% to 25% by weight styrene or aliphatic or aromatic substituted styrene and 95% to 75% by weight based on total monomer content of cyclic diolefin component comprising at least 50% by weight dicyclopentadiene (e.g., see U.S. Pat. No. 6,825, 291). This procedure of sequential monomer addition has been used to control the molecular weight of the hydrocarbon resin. Not only is this process cumbersome, but can result in broad polydispersity of the hydrocarbon resin. Table 1 below summarizes the comparative results obtained.

TABLE 1

Sample	Reference	Mn (g/mol)	T _g (° C.)	HAr (%)	MMA Cloud Point
1	PR-100	474	83	0%	70.8
2	E5415	386	61	0%	65.7
3	E5340	422	86	0%	64.2
4	E5320	398	67	0%	63.3
5	E5637	527	79	5%	61.8

Example 2: Analysis of the Invention Specific Hydrocarbon Resins

Hydrocarbon resin (HR) samples Nos. 1 to 4 were prepared by varying the feed streams in a thermal polymeriza-

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tion unit known to achieve a certain tackifier cloud point. After processing in the thermal polymerization unit, the tackifiers were nitrogen-stripped at 200° C. The properties of the hydrocarbon resins are provided in the Tables 2A, 2B, 3A and 3B below. The resins described herein can be produced by known methods (e.g., see the Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. 13, pp. 717-744). One method is to thermally polymerize petroleum fractions. Polymerization can be batch, semi-batch or continuous. Thermal polymerization is often carried out at a temperature between 160° C. and 320° C., for example, at 260° C. –280° C., for a period of 0.5 to 9 hours, and often 1.0 to 4 hours. Thermal polymerization is usually carried out in presence or absence of inert solvent.

The inert solvent can have a boiling point range from 60° C. to 260° C. and can be selected from isopropanol, toluene, heptane, Exxsol™ or Varsol™ or base “White spirit” from 2 wt. % to 50 wt. %. Solvents can be used individually or in combinations thereof.

The hydrocarbon resin produced can be optionally dissolved in an inert, de-aromatized or non-de-aromatized hydrocarbon solvent such as Exxsol™ or Varsol™ or base “White spirit” in proportions varying from 10% to 60% and for example in the region of 30% by weight polymer. Hydrogenation is then conducted in a fixed-bed, continuous reactor with the feed flow either in an up flow or downflow liquid phase, or trickle bed operation.

Hydrogenation treating conditions generally include reactions ranging in temperature of from 100° C. to 350° C., from 150° C. to 300° C., and from 160° C. to 270° C. The hydrogen pressure within the reactor should not exceed more than 2000 psi, for example, no more than 1500 psi, and/or no more than 1000 psi. The hydrogenation pressure is a function of the hydrogen purity and the overall reaction pressure should be higher if the hydrogen contains impurities to give the desired hydrogen pressure. Typically, the optimal pressure used is between 750 psi and 1500 psi, and/or between 800 psi and 1000 psi. The hydrogen to feed volume ratio to the reactor under standard conditions (25° C., 1 atm pressure) typically can range from 20 to 200. Further exemplary methods for preparing the hydrocarbon resins described herein are generally found in U.S. Pat. No. 6,433,104.

Tables 2A and 2B below include the feed streams, polymerizing conditions and properties obtained for comparative hydrocarbon resins.

TABLE 2A

Hydrocarbon Resins				
Feed streams	HR 1	HR 2	HR 3	HR 4
Cyclics (wt %)	66.5	60	49.9	67.9
Olefin Aromatics (wt %)	0	0	0	0
Substituted benzene (wt %)	0	0	0	0
Aromatic distillation cut (wt %)	0	25	0	0
MCPD (wt %)	3.5	3.0	0.1	0.1
Solvent (wt %)	30	12	50	32
Reaction temperature (° C.)	265	260	275	275
Reaction time (min)	60	60	60	60

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TABLE 2B

Present hydrocarbon resin Properties Measured After Hydrogenation				
	HR 1	HR 2	HR 3	HR 4
HR Softening Point (° C.)	150	144	>150	>150
HR Tg (° C.)	99	91	103	112
MMAP cloud point (° C.)	57.5	54.3	49.3	32.6
Mn (g/mol)	431	457	396	421
Mw/Mn (MWD)	1.8	1.7	1.5	1.8
Aromatic H (H Ar) in mol %	0.6	5	0.3	0.1

As provided in Tables 3A and 3B, comparative examples 2A, 2B & 2C were prepared with varying methyl cyclopentadiene (MCPD) derived content such as MCPD and “MCPD derived content”. With the increase in MCPD content, the Mn increases but without change in Tg. MCPD-derived content increases number of chains, which is measured by increase in Mn, but promotes branching. Therefore, no change of Tg was observed in the comparative examples.

On the other hand, the present hydrocarbon resin has lower amounts of MCPD and MCPD derived content, specifically, 0.1 wt. % to 15 wt. % and/or 0.1 wt. % to 5 wt. % of the total weight of the hydrocarbon resin. The hydrocarbon resin can be a hydrogenated cyclopentadiene or a hydrogenated cyclopentadiene derivative with or without the aromatic monomer (olefin-aromatics, substituted benzene and aromatic distillation cut).

TABLE 3A

Comparatives			
Feed streams	Comp. 2A	Comp. 2B	Comp. 2C
Cyclics	46	52	58
Olefin Aromatics	0	0	0
Substituted benzene	0	0	0
Aromatic distillation	25	25	25
MCPD	14	8	2
Solvent	15	15	15
Reaction temperature (° C.)	265	260	275
Reaction time (min)	45	45	45

TABLE 3B

Comparatives Properties Measured After Hydrogenation			
HR	Comp. 2A	Comp. 2B	Comp. 2C
HR Softening Point (° C.)	120	117	121
HR Tg (° C.)	70	68	70
Mn (g/mol)	374	357	346
Mw/Mn (MWD)	1.5	1.5	1.5
Aromatic H (H Ar) in mol %	5.9	5.8	5.6

FIG. 1 is a graph showing the Tg and H Ar relationship of the present hydrocarbon resins, comparative resins and commercial prior art elastomeric compositions. FIG. 2 is a graph showing the Tg and Mn relationship of the present HRs, comparative resins and prior art comparative elastomeric compositions.

Example 3: Exemplary Rubber Compositions

Rubber compositions are manufactured with introduction of all of the constituents onto an internal mixer, with the exception of the vulcanization system. The vulcanization

agents (sulfur and accelerator) are introduced onto an external mixer at low temperature (the constituent rolls of the mixer being at 30° C.).

The object of the examples presented in Table 4 is to compare the different rubber properties of control compositions (T1 to T5) to the properties of composition having the present hydrocarbon resin 1 to 4 (C₁ to C₄). The properties measured, before and after curing, are presented in Table 5.

TABLE 4

Rubber Composition of Different hydrocarbon resins									
	T1	T2	T3	T4	T5	C1	C2	C3	C4
SBR (1)	100	100	100	100	100	100	100	100	100
Carbon black (2)	4	4	4	4	4	4	4	4	4
Silica (3)	130	130	130	130	130	130	130	130	130
PR 100	88	—	—	—	—	—	—	—	—
E5415	—	88	—	—	—	—	—	—	—
E5340	—	—	88	—	—	—	—	—	—
E5320	—	—	—	88	—	—	—	—	—
E5637	—	—	—	—	88	—	—	—	—
HR 1	—	—	—	—	—	88	—	—	—
HR 2	—	—	—	—	—	—	88	—	—
HR 3	—	—	—	—	—	—	—	88	—
HR 4	—	—	—	—	—	—	—	—	88
Anti-oxidant (4)	6	6	6	6	6	6	6	6	6
Coupling agent (5)	13	13	13	13	13	13	13	13	13
DPG (6)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid (7)	3	3	3	3	3	3	3	3	3
ZnO (8)	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Accelerator (9)	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
Soluble sulfur	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7

(1) SBR of Tg = −88° C. as disclosed in the examples of WO2017/168099
(2) Carbon black, ASTM N234 grade
(3) Silica, “Zeosil 1165 MP” from Solvay, HDS type
(4) N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (“Santoflex 6-PPD”) from Flexsys and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ)
(5) Coupling agent: “Si69” from Evonik-Degussa
(6) Diphenylguanidine, “Perkacit DPG” from Flexsys
(7) Stearin, “Pristerene 4931” from Uniqema
(8) Zinc oxide, industrial grade-Umicore
(9) N-Cyclohexyl-2-benzothiazolesulfenamide (“Santocure CBS” from Flexsys)

TABLE 5

Rubber Composition Properties										
	T1	T2	T3	T4	T5	C1	C2	C3	C4	
G* 10% at 23° C. (base 100)	100%	91%	101%	91%	96%	149%	111%	171%	133%	
G* 10% at 40° C. (base 100)	100%	96%	99%	98%	96%	153%	116%	171%	123%	

TABLE 6

Rubber Composition of Different hydrocarbon resins			
	T6	C5	C6
BR (10)	100	100	100
Carbon black (2)	4	4	4
Silica (3)	130	130	130
PR-100	95.4	—	—
HR 3	—	95.4	—
HR 4	—	—	95.4

TABLE 6-continued

Rubber Composition of Different hydrocarbon resins			
	T6	C5	C6
Antioxydant (4)	8.85	8.85	8.85
Coupling agent (5)	13	13	13
DPG (6)	2.4	2.4	2.4
Stearic acid (7)	3	3	3
ZnO (8)	0.9	0.9	0.9
Accelerator (9)	2.3	2.3	2.3
Soluble sulfur	0.7	0.7	0.7

(10) BR: polybutadiène «CB24» from Lanxess; 96% of 1,4-cis; Tg = −107° C.

TABLE 7

Rubber Composition Properties			
	T6	C5	C6
G* 10% at 23° C. (base 100)	100%	103%	148%
G* 10% at 40° C. (base 100)	100%	104%	150%

TABLE 8

Rubber Composition of Different hydrocarbon resins			
	T7	C7	C8
SBR (11)	100	100	100
Carbon black (2)	3	3	3
Silica (3)	70	70	70
PR-100	39		
HR 3		39	
HR 4			39
Antioxydant (4)	6	6	6
Coupling agent (5)	5.6	5.6	5.6
DPG (6)	1.6	1.6	1.6
Stearic acid (7)	2	2	2
ZnO (8)	0.9	0.9	0.9
Accelerator (9)	2.45	2.45	2.45
Soluble sulfur	1	1	1

(11) Non-functionalized SBR, having 26.5% by weight of styrene unit relative to the total weight of the copolymer and 24 mol % of unit 1, 2 of butadiene relative to the butadiene part and having a glass transition temperature, Tg, of −48° C.

TABLE 9

Rubber Composition Properties			
	T7	C7	C8
G* 10% at 23° C. (base 100)	100%	102%	111%
G* 10% at 40° C. (base 100)	100%	101%	105%

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Relative to the control compositions, it is noted that the compositions T1, T6 and T7, which are not in accordance with hydrocarbon resins described herein, respectively serve as base 100 for comparing the performance of the other compositions. It is noted that only the compositions C₁ to C₈ according to the invention enable improvement in road handling performance.

The invention claimed is:

1. A tire comprising a rubber composition based on at least an elastomer and a hydrocarbon resin,

wherein the hydrocarbon resin is based on a cyclic monomer selected from the group consisting of a distillation cut from a petroleum refinery stream, C₄, C₅ or C₆ cyclic olefins and mixtures thereof,

wherein the hydrocarbon resin comprises the cyclic monomer in an amount between 20 wt. % and 99 wt. %, and

wherein the hydrocarbon resin has a number average molecular weight (Mn) of between 150 and 800 g/mol, and a content of aromatic protons (H Ar, expressed in mol %), a glass transition temperature (Tg, expressed in ° C.), and a number average molecular weight (Mn, expressed in g/mol) that are represented by:

- (1) $H\ Ar \leq 6\ \text{mol}\ \%$,
- (2) $Tg \geq 95 - 2.2 * (H\ Ar)$, and
- (3) $Tg \geq 125 - (0.08 * Mn)$.

2. The tire according to claim 1, wherein the cyclic monomer is selected from the group consisting of cyclopentene, cyclopentadiene, dicyclopentadiene, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, methylcyclopentadiene, di(methylcyclopentadiene) and mixtures thereof.

3. The tire according to claim 1, wherein the hydrocarbon resin comprises methylcyclopentadiene in an amount between 0.1 wt. % and 15 wt. %.

4. The tire according to claim 1, wherein the hydrocarbon resin is further based on an aromatic monomer.

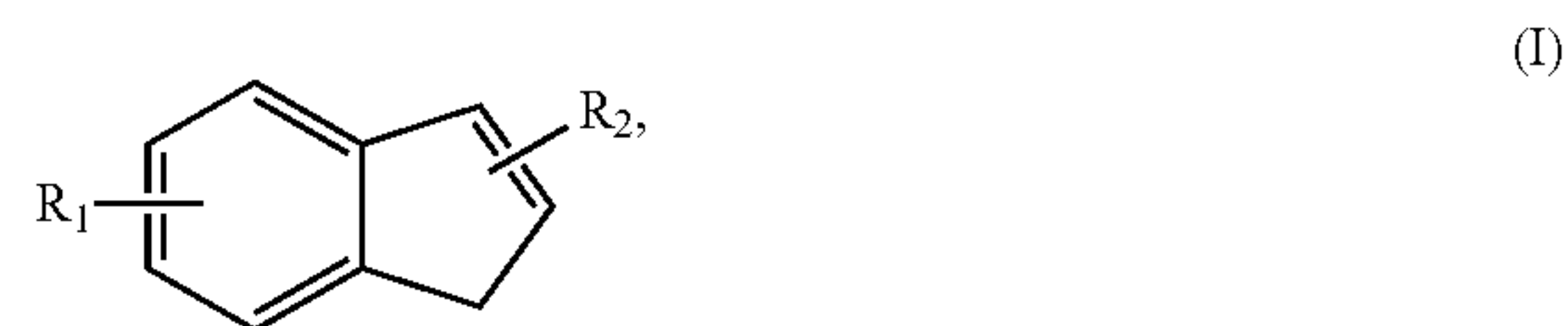
5. The tire according to claim 4, wherein the aromatic monomer is selected from the group consisting of olefin-aromatic compounds, aromatic distillation cuts and mixtures thereof.

6. The tire according to claim 5, wherein the aromatic monomer is an aromatic distillation cut.

7. The tire according to claim 5, wherein the aromatic monomer comprises an olefin-aromatic compound selected from the group consisting of indene derivatives, vinylaromatic compounds and mixtures thereof.

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8. The tire according to claim 7, wherein the aromatic monomer comprises an indene derivative of Formula (I)



wherein R₁ and R₂ represent, independently of one another, a hydrogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group or an arylalkyl group.

9. The tire according to claim 7, wherein the aromatic monomer comprises a vinylaromatic compound of Formula (II)



wherein R₃ and R₄ represent, independently of one another, a hydrogen atom, an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group or an arylalkyl group.

10. The tire according to claim 1, wherein the hydrocarbon resin has at least one of the following additional features:

- a MMAP cloud point of between 10° C. and 60° C.;
- a number average molecular weight (Mn) of between 250 and 600 g/mol;
- a glass transition temperature (Tg) of 95° C. or more; and
- a content of aromatic protons (H Ar) of 3 mol % or less.

11. The tire according to claim 1, wherein a content of the hydrocarbon resin is within a range extending from 15 to 150 phr.

12. The tire according to claim 1, wherein the at least one elastomer comprises an elastomer having a glass transition temperature Tg of less than -40° C. in an amount greater than or equal to 60 phr.

13. The tire according to claim 1, wherein the at least one elastomer comprises an elastomer selected from the group consisting of essentially unsaturated diene elastomers in an amount greater than or equal to 60 phr.

14. The tire according to claim 1, wherein the rubber composition further comprises a reinforcing filler.

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